1 413 513

PATENT SPECIFICATION

(11) 1 413 513

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(52) Index at acceptance
C4P D1M D1X1
C2C 220 222 227 22Y 30Y 313 314 31Y 328 332 338 364 365 366 367 36Y 624 633 662 682 687 689 699 710 MG

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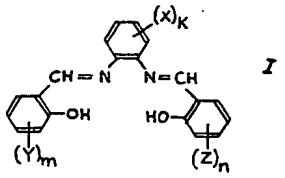
(54) BISAZOMETHINE COMPOUNDS

(71) We, CIBA-GEIGY AG., a Swiss Body Corporate, of Basle 4002, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a new class of bisazomethines of use in the production of metallised bisazomethine compounds of value as pigments.

The present invention provides a compound having the formula:—

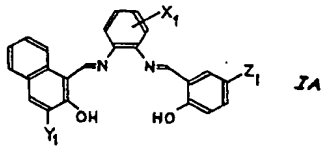


I

wherein X and Y are the same or different and each is hydrogen or a non-water-solubilising group and Z has the same significance as X and Y, two adjacent X groups or two adjacent Y groups or two adjacent Z groups may form a fused arylene ring, which may itself carry further non-water-solubilising substituents, and k, m and n are the same or different and each is an integer from 1 to 4.

Examples of non-water-solubilising X, Y and Z include halogen, alkyl and alkoxy groups having from 1 to 4 carbon atoms in the alkyl moiety, nitro and carboxy groups, arylazo groups and fused arylene residues.

A preferred sub-group of compounds formula I are those having the formula:—

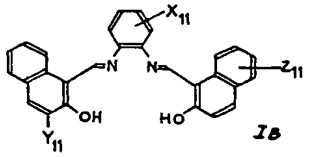


IA

wherein X_1, Y_1 and Z_1 are the same or different and each is hydrogen or a non-water-solubilising group.

A preferred instance of the group X_1 is a halogen atom, especially a chlorine atom, or an alkyl group having from 1 to 4 carbon atoms, especially a methyl group; preferably Y_1 is hydrogen or a carboxy group; and preferably Z_1 is a halogen atom especially a bromine atom.

A further preferred sub-group of compounds of formula I are those having the formula:—

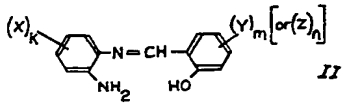


IB

wherein X_{11}, Y_{11} and Z_{11} are the same or different and each is hydrogen or a non-water-solubilising group.

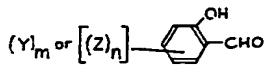
Preferred instances of group X_{11} are an alkyl group having from 1 to 4 carbon atoms, a nitro group, a halogen atom or a phenoxy group; preferably Y_{11} is hydrogen or a carboxy group; and preferably Z_{11} is hydrogen.

The present invention also provides a process of producing a compound of formula I comprising condensing a compound of formula:—



II

wherein X, Y, Z, k, m and n have their previous significance, with an *o*-hydroxy aldehyde having the formula:—



III

wherein Y, Z, m and n have their previous significance.

The condensation step of the reaction of compounds II and III may be effected in solution or in a finely-dispersed suspension with good agitation using either water or an organic solvent as the reaction medium. The reaction is conveniently effected at an elevated temperature, usually between 50° C and the reflux temperature depending upon the reactants and the solvent used. Preferably, the progress of the reaction is monitored to ensure that the reaction is proceeding at a satisfactory rate and that the end product is not being rendered impure by side reactions such as disproportionation.

The starting-materials of formula II and their mode of manufacture are described and claimed in our co-pending British Patent Application No. 34730/74 (Serial No. 1,413,514).

The starting-materials of formula III are well-known *per se*.

The compounds of formula I of the present invention are useful as intermediates for the metallised bisazomethine pigments described and claimed in our co-pending British Patent Application No. 12822/72.

Some Examples will now be given; parts and percentages are expressed by weight unless otherwise stated.

Example 1.

(a) 86.0 Parts of 2 - hydroxy - 1 - naphthaldehyde and 54.0 parts of *o* - phenylene diamine were dispersed in 750 parts of water containing 2 parts of a commercial nonionic surfactant by stirring for 15 minutes at room temperature. 20.0 parts of sodium hydroxide in 250 parts of water was added to the suspension over one minute to give a thick, bright yellow suspension which was stirred at room temperature for 15 minutes then 76.0 parts of sodium bisulphite were added and stirring continued for 2 hours, then filtered, and the filter-cake washed with 10,000 parts of water, until the washes were free of sulphate, giving a paste containing 115 parts (88%) of a bright yellow solid. A sample of this paste was dried and found to have a melting-point of 160—1° C.

(b) 24.0 Parts of the monoazomethine product of part (a) and 23.6 parts of 1 - formyl - 2-hydroxy - 3 - naphthoic acid were stirred and heated to reflux in 500 parts of ethanol for 2 hours. The resultant orange suspension was filtered, the filter-cake washed with 500 parts of ethanol and dried, producing 27.5 parts of an orange solid m.p. 269—70° C.

By substituting an equivalent amount of the appropriate monoazomethine and *o* - hydroxy aldehyde, the products in the following Table II were obtained. Table I also gives the appropriate colour, yield and melting point of the various products.

TABLE I

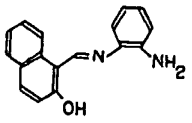
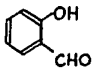
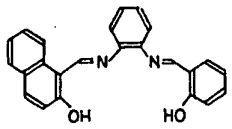
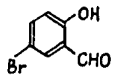
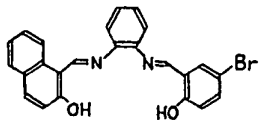
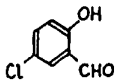
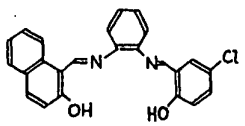
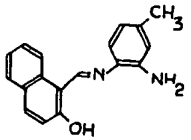
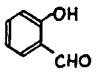
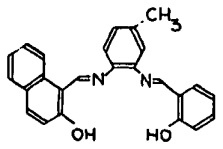
Example	Azomethine	o-hydroxyaldehyde	Product	Colour	% Yield	m.p. °C
2				Yellow	60	204– 5
3				Yellow	55	205– 6
4				Yellow	87	184– 6
5				Orange	62	170– 4

TABLE I (Continued)

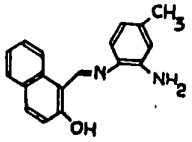
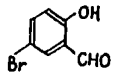
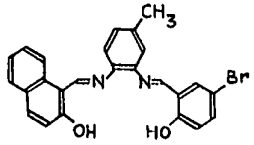
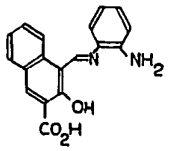
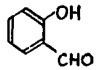
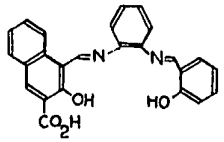
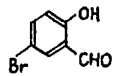
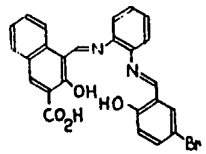
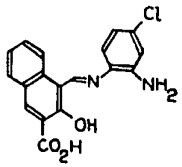
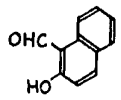
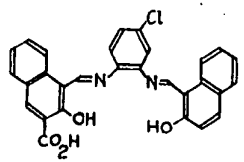
Example	Azomethine	*o*-hydroxyaldehyde	Product	Colour	% Yield	. m.p. °C
6				Yellow	56	190– 4
7				Orange	79	225– 8
8				Red	50	257– 6
9				Orange	81	–

TABLE I (Continued)

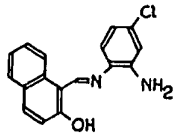
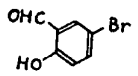
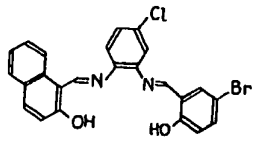
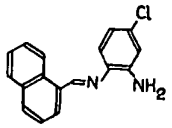
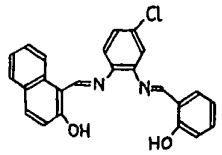
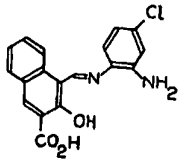
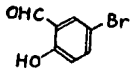
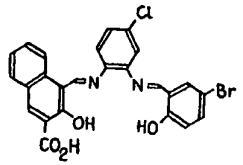
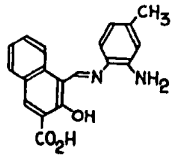
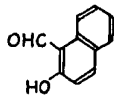
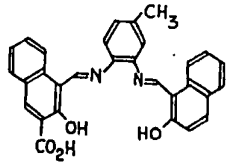
Example	Azomethine	o-hydroxyaldehyde	Product	Colour	% Yield	m.p. °C
10				Orange	90	231–32
11				Orange	80	–
12				Orange	75	277–78
13				Orange	92	–

TABLE I (Continued)

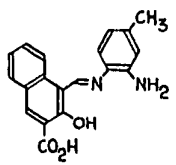
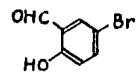
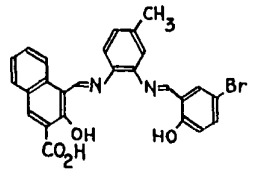
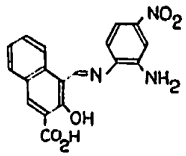
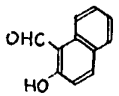
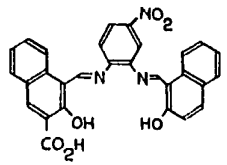
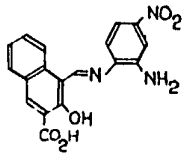
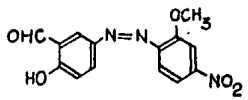
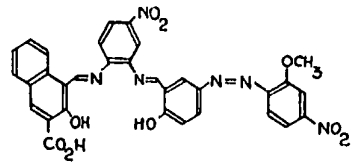
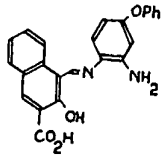
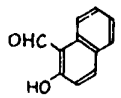
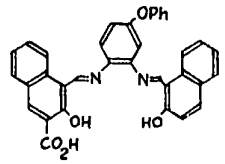
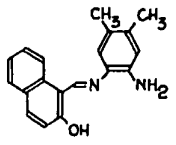
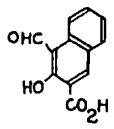
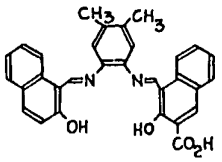
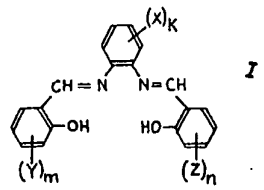
Example	Azomethine	o-hydroxyaldehyde	Product	Colour	% Yield	m.p. °C
14				Red-brown	60	180–83
15				Red	75	
16				Orange	95	
17				Orange	60	

TABLE I (Continued)

Example	Azomethine	*o*-hydroxyaldehyde	Product	Colour	% Yield	m.p. °C
18				Orange-yellow	91	

WHAT WE CLAIM IS:—

1. A compound having the formula:

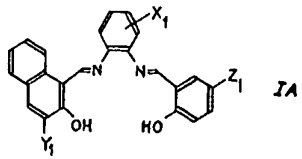


I

wherein X and Y are the same or different, and each is hydrogen or each represents a non-water-solubilising group, and Z has the same significance as X and Y, or two adjacent X groups or two adjacent Y groups or two adjacent Z groups form a fused arylene ring which may itself carry further non-water-solubilising substituents, and k, m and n are the same or different and each is an integer from 1 to 4.

2. A compound as claimed in claim 1 wherein the non-water-solubilising groups X, Y and Z are halogen, alkyl or alkoxy groups having from 1 to 4 carbon atoms in the alkyl moiety, nitro, carboxy or arylazo groups or fused arylene residues.

3. A compound as claimed in claim 1 or 2 having the formula:—



IA

wherein X_1, Y_1 and Z_1 are the same or different and each is hydrogen or a non-water-solubilising group.

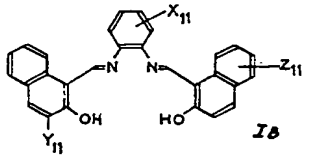
4. A compound as claimed in claim 3 wherein X_1 is halogen or an alkyl group having from 1 to 4 carbon atoms, Y_1 is hydrogen or a carboxy group and Z_1 is halogen.

5. A compound as claimed in claim 4

wherein X_1 is a chlorine atom or a methyl group.

6. A compound as claimed in claim 4 wherein Z_1 is a bromine atom.

7. A compound as claimed in claim 1 or 2 having the formula:—



Ia

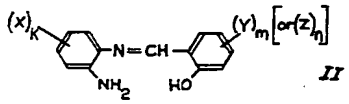
wherein X_{11}, Y_{11} and Z_{11} are the same or different and each is hydrogen or a non-water-solubilising group.

8. A compound as claimed in claim 7 wherein X_{11} is an alkyl group having from 1 to 4 carbon atoms, a nitro group, a halogen atom or a phenoxy group, Y_{11} is hydrogen or a carboxy group and Z_{11} is hydrogen.

9. A compound of formula I, as claimed in claim 1, substantially as described with reference to any of Examples 1 to 8.

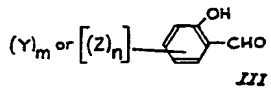
10. A compound of formula I as claimed in claim 1 substantially as described with reference to any of Examples 9 to 19.

11. A process for the production of a compound of formula I as defined in claim 1 comprising reacting a compound having the formula:—



II

wherein X, Y, Z, k, m and n are as defined in claim 1 with an *o*-hydroxy aldehyde having the formula:—



III

wherein Y, Z, m and n are as defined in claim 1.

12. A process as claimed in claim 11, wherein the reaction is effected in solution or in a finely-dispersed suspension with good agitation, using water as the reaction medium.

13. A process as claimed in claim 11 or 12, wherein the reaction is effected at a temperature between 50° C and the reflux temperature of the mixture.

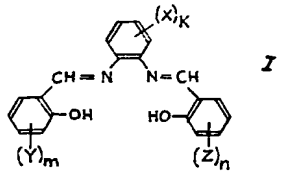
14. A process as claimed in claim 11, substantially as described with reference to any of Examples 1 to 8.

15. A process as claimed in claim 11, substantially as described with reference to any of Examples 9 to 19.

16. A compound of formula I as claimed in claim 1 when produced by a process claimed in any of claims 11 to 14.

17. A compound of formula I as claimed in claim 1 when produced by a process claimed in claim 15.

18. A compound having the formula



I

wherein X and Y are the same or different and each is hydrogen or each represents a non-water-solubilising group and Z has the same significance as X and Y, two adjacent X groups or two adjacent Y groups or two adjacent Z groups may form a fused arylene ring, with the proviso that Y and Z cannot be identical, and k, m and n are each 1, 2, 3 or 4.

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